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COMMENTS ON "ION-ION AND ION-WATER INTERACTIONS AT HIGH PRESSURE"

[M. Nakahara and J. Osugi, *Rev. Phys. Chem. Japan*, **45**, 69 (1975)]

BY S. D. HAMANN

A recent, very interesting, review on electrolyte solutions under pressure by Nakahara and Osugi[1] contained two criticisms of the work of the writer and his colleagues, which were minor ones but nevertheless call for some reply.

First, Nakahara and Osugi[1] criticized Hamann and Linton[2] for using formula (4)*, or its equivalent (5), to represent the pressure dependence of ionic activity coefficients γ. They suggested that it gives values of the ratio $\log\gamma^{(p)}/\log\gamma^{(1)}$ that are substantially lower—by about 8% at 5 kbar—than values calculated directly from the limiting Debye-Hückel relationship. However, the values that Nakahara and Osugi listed in the third column of their Table 1, as being derived from (5), are wrong. The correct values are as follows:

Pressure/kbar	0.5	1	2	3	4	5
$\log\gamma^{(p)}/\log\gamma^{(1)}$ from eq. (5)	0.977	0.956	0.919	0.887	0.860	0.835

These are within 0.8% of the limiting Debye-Hückel values and, in the pressure range in which Hamann and Linton used them they are within 0.04%. Hamann and Linton[2] were right in saying that "the term involving b . . . corrects for the non-linearity of the pressure dependence of the dielectric constant and density". Formulae (4) and (5) are more convenient to use than (3) and are more accurate than Nakahara and Osugi's empirical approximation (10).

Nakahara and Osugi's second criticism[1] was a repetition of earlier remarks by Nakahara *et al.*[3] to the effect that the high pressure conductivity values of Buchanan and Hamann[4] for aqueous solutions of KCl "are too low". Although the writer claims no high accuracy for the data of Buchanan and Hamann, he has shown elsewhere[5] that there is considerable independent evidence (not cited by Nakahara and Osugi in their Table 2) indicating that the values of Buchanan and Hamann are not too low, but that those of Nakahara *et al.*[3] are too high.

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* The numbering of formulae is the same as that of Nakahara and Osugi[1].

1) M. Nakahara and J. Osugi, *This Journal*, **45**, 69 (1975)
2) S. D. Hamann and M. Linton, *J. C. S. Faraday Trans. I*, **70**, 2239 (1974)
3) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **42**, 12 (1972)
4) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953)
5) S. D. Hamann, in "Modern Aspects of Electrochemistry", Vol. 9, Chap. 2, p. 66 (Ed. B. E. Conway and J. O'M. Bockris, Plenum, New York, 1974)